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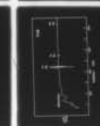
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## RECENT PROGRESS IN SURFACE ANALYSIS

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The most basic requirements in surface analysis are to identify the chemical constituents and to determine their structural arrangement. Progress in chemical analysis has been rapid since the introduction of Auger electron spectroscopy, but the extreme complexity of low energy electron diffraction analysis has limited surface crystallography to a few relatively simple structures. It may, however, be possible to extract structural information, even from relatively disordered surfaces, using extended fine structure techniques. Fine structure variations have been observed to extend hundreds of electron volts above appearance potential thresholds. This structure is analogous to extended X-ray absorption fine structure (EXAFS), and can be interpreted in terms of interatomic distances in the surface region. The recent development of extended appearance potential fine structure (EAPFS) analysis is reviewed. The technique is of potential benefit in the resolution of LEED analysis problems on single crystal surfaces, as well as in the study of less ideal surfaces. The present limitations of the technique are stressed and analytical and experimental approaches to minimizing these limitations are discussed.

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## INTRODUCTION

The history of surface physics is much more a record of the development of new analytical techniques for the characterization of surfaces, than of the development of great unifying theories. The most basic requirements in this characterization are to identify the chemical constituents of the surface region, and to determine their structural arrangement.<sup>1</sup> Progress in chemical identification has been rapid since the introduction by Harris of Auger electron spectroscopy (AES) just ten years ago.<sup>2</sup> Surface crystallography, on the other hand, began more than half a century ago with the discovery of low energy electron diffraction (LEED) by Davisson and Germer.<sup>3</sup> It was predicted that LEED would in time provide a crystallography of the surface as precise as X-ray diffraction has of the bulk. It must be acknowledged, however, that this prediction has yet to be realized. Although diffraction from a number of clean single-crystal metal surfaces and a handful of chemisorption systems has been satisfactorily described, the complications of multiple-scattering and inelastic collision damping of the elastic wavefront make it uncertain whether it will prove fruitful to extend LEED analysis to more complicated surfaces.

Not long after the discovery of electron diffraction, Krönig<sup>4</sup> pointed out that the fine structure in the absorption cross section of X-rays in solids can be accounted for by diffraction of the photoelectrons ejected from the core level. This oscillatory structure, which may extend for hundreds of electron volts above an absorption edge, results from interference of the outgoing spherical wave of the ejected core-state electron with backscattered components from neighbors of the absorbing atom. Apart from corrections due to

the scattering phase shifts, the periodicities in the absorption cross section vs. photoelectron momentum are the reciprocal interatomic spacings. This simple picture holds best at energies far above threshold where multiple scattering of the outgoing electron is less important. Interest in this phenomenon was renewed in 1971 when Sayers, Stern and Lytle<sup>5</sup> demonstrated that a Fourier transformation of the EXAFS spectrum would directly yield the distances between the absorbing atom and its nearby neighbors.

Essentially identical structure may be observed with electron excitation. Ritsko, Schnatterly and Gibbons<sup>6</sup> observed fine structure in core level electron energy loss spectra of 300 keV electrons transmitted through thin foils. They took advantage of the fact that, for small momentum transfer, dipole selection rules apply to electron excitation. This has the important consequence that, for the interpretation of K edge fine structure, only a single phase-shift function is needed, and there is no mixing of partial waves. The results are therefore directly comparable to X-ray spectra.

These techniques are, of course, relatively insensitive to the surface. Chemisorption has, nevertheless, been studied on a few carefully chosen high surface area materials. Thus for example the adsorption of  $\text{Br}_2$  on Grafoil was studied by conventional absorption methods.<sup>7</sup> An approach better suited to surface studies is to use an indirect measure of X-ray absorption. Peterson and Kunz<sup>8</sup> demonstrated that extended fine structure could be measured above the 2p excitation edges of Na and Al by monitoring the total yield of photoelectrons as a function of the frequency of incident synchrotron radiation. The excitation of a core state is signaled by an increase in electron emission due to Auger recombination of the core hole. This technique has the distinct advantage over conventional X-ray absorption that it does not require thin foil samples.

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Nevertheless, the resulting spectra are more nearly indicative of the bulk structure than the surface, since the measured increase in yield consists mostly of low-energy secondary electrons, and not the Auger electrons themselves.

Landman and Adams<sup>9</sup> pointed out that by using an electron spectrometer to select a particular Auger line, the technique could be made highly surface sensitive, since only those Auger electrons originating very near the surface could escape without inelastic scattering. This approach was used by Citrin and Eisenberger<sup>10</sup> to study the adsorption of  $I_2$  on Ag(111). The high intensity of a synchrotron X-ray source was necessary to enable the measurements to be completed in the limited time available for experiments on clean surfaces. This, in effect, restricts the use of this technique to those few groups that are able to utilize the large electron-positron storage rings at the Stanford Linear Accelerator (SLAC) in Palo Alto, and the Deutsches Elektronen-Synchrotron (DESY) in Hamburg. It was pointed out as early as 1971, however, by Houston and Park,<sup>11</sup> that extended fine structure could also be observed above the thresholds for electron scattering from core states using appearance potential spectroscopy (Fig. 1).

The critical or "appearance" potentials for the excitation of characteristic X-rays by electron bombardment were widely used in the late 1920's to construct X-ray energy level diagrams of the elements. The method consisted of detecting abrupt, albeit small, changes in the slope of the total X-ray yield of an anode as a function of the applied potential. The emission from a metal photocathode exposed to the X-rays was used as a measure of the total yield. The method was not particularly sensitive because of the large bremsstrahlung background

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that tends to obscure the subtle changes in total yield that result from the excitation of characteristic radiation. Shinoda, Suzuki and Kato<sup>12</sup> demonstrated that it is possible to suppress the bremsstrahlung without a dispersive analyzer by electronically differentiating the yield. Soft X-ray appearance potential spectroscopy was developed as a practical technique for surface analysis by Park and Houston.<sup>13</sup>

In the energy range of interest for surface studies, a core hole is much more likely to recombine by an Auger process than by X-ray emission, and it is possible to detect the appearance potentials in the derivative of the secondary electron yield. The spectra obtained are essentially the same as those obtained by the soft X-ray technique.<sup>14</sup> Most of the electrons contributing to the increase in secondary electron yield at the threshold for core scattering have energies below 30 eV, and result from secondary processes following Auger recombination of the core hole.<sup>15</sup> The elastic yield, however, decreases at the threshold due to opening a new channel for inelastic scattering.<sup>16</sup> Although there are a number of possible complications involved in attempting to utilize electron excitation to obtain interatomic spacings,<sup>17</sup> none of these complications appear to be crucial, and the technique has been shown to be capable of extracting nearest neighbor distances for several clean metal surfaces.<sup>18,19</sup> This has significant implications for LEED analysis of single crystal surfaces, since a knowledge of the nearest-neighbor spacing would enormously reduce the number of model calculations. More significantly, however, it provides a structural characterization based on short range order. This should make it possible to study structures of less ideal surfaces. Indeed, many technologically interesting materials are not available in single crystal form.

In this paper, progress in extended fine structure analysis of surfaces using electron excitation will be reviewed. The limitations of the technique will be stressed and analytical and experimental approaches to minimizing these limitations will be discussed.



### APPEARANCE POTENTIAL SPECTROSCOPY

Let us first review briefly the appearance potential technique, as it compares to X-ray absorption. The two experiments are contrasted in the energy level diagrams of Fig. 2.

In X-ray absorption an incident photon can be absorbed by a core electron if its energy  $h\nu$  exceeds the core state binding energy  $E_B$ . The ejected core electron will have an energy  $\epsilon = h\nu - E_B$  relative to the Fermi level of the sample. If dipole selection rules are satisfied, the probability that the X-ray will be absorbed depends on the states available at  $\epsilon$ . Near the edge, this may be thought of as the usual plane wave density of states modulated by the oscillator strength of the transition, which is presumably a slowly varying function of  $\epsilon$ . It is convenient to lump these terms together and speak of a transition density  $N_Y(E)$ . The absorption of an X ray is signaled by a decrease in transmission through the sample, an increase in electron emission, or an increase in characteristic emission associated with recombination of the core hole.

There is also a threshold energy for inelastic electron scattering from a core state, when the incident electron energy  $E_0$  is equal to  $E_B$ . The incident electron, however, need not give up all its energy to the core electron and the excitation probability above the threshold depends on the states available to two electrons. To a first approximation this probability will vary as the self convolution of the one-electron transition density  $N_Y(\epsilon)$  that describes X-ray absorption:

$$N_B(\epsilon) = \int_0^\infty N_Y(\epsilon') N_Y(\epsilon - \epsilon') d\epsilon' \quad (1)$$

This integral has the effect of obscuring the structure contained in  $N_Y(\epsilon)$ .



For metals, however, in which the transition density increases abruptly at the Fermi discontinuity, the structure can be recovered by examining the derivative of  $N_{\beta}(\epsilon)$ .

$$\frac{dN_{\beta}(\epsilon)}{d\epsilon} = \int_0^{\infty} \frac{dN_Y(\epsilon')}{d\epsilon'} N_Y(\epsilon - \epsilon') d\epsilon' \quad (2)$$

where the lower limit is taken just below the edge such that  $N_Y(0) = 0$ . To the extent that  $\frac{dN_Y(\epsilon)}{d\epsilon}$  is dominated by the Fermi discontinuity, it can be approximated as a delta function:

$$\frac{dN_Y(\epsilon)}{d\epsilon} \approx N_F \delta(\epsilon) \quad , \quad (3)$$

where  $N_F$  is a constant representing the increase in transition density at the threshold. Thus the transition density function for electron excitation  $N_{\beta}(\epsilon)$  is related approximately to the transition density for X ray absorption  $N_Y(\epsilon)$  by

$$\frac{dN_{\beta}(\epsilon)}{d\epsilon} = N_F N_Y(\epsilon). \quad (4)$$

This approximation is best for free-electron like metals, in which case  $N_Y(\epsilon)$  exhibits a step-like increase at the excitation edge.

Appearance potential spectroscopy has been used to follow changes in the local electronic structure of surface metal atoms caused by chemisorption of light gases.<sup>20</sup> The advantage of such a core level probe of the electronic structure is that the core electron wave functions overlap a narrow region of the conduction band, thus providing a very local view of the electronic structure. It is therefore possible to examine separately the local density of states

associated with different elements on the same surface.

Near the threshold, the transition density is usually compared to the plane wave density of states of the material.<sup>21</sup> This is probably not a bad approximation near the edge where the wavelength of the electron is very long. In fact, however, the localization of the core hole means that the electrons must be treated as outgoing spherical waves, and the "local" density of states can be thought of as arising from the interference properties of these spherical waves. Thus, the assertion that the near-edge structure is a consequence of density of states effects, whereas the extended structure is caused by interference may be misleading,<sup>22</sup> it is just that it is convenient to use different approximations in the near and extended regions.

## EXPERIMENTAL

For incident electron energies in the energy range below perhaps 2keV, the short mean free path for inelastic scattering limits the sampling depth of appearance potential spectra to the outermost several atomic layers. If the creation of a core hole is detected as an increase in the soft X-ray yield, the technique is termed soft X-ray appearance potential spectroscopy (SXAPS). The photocurrent from a metal surface exposed to X rays from the sample can serve as a measure of the total X-ray yield.<sup>23</sup> Such a spectrometer is trivial to construct. The efficiency of the photoelectric detection scheme, however, is quite low. To compensate, most researchers have used incident electron currents of several milliamps. These high currents are easily achieved since a focused beam is not required, but fragile surfaces may be destroyed by such a bombardment.

More sensitive detection schemes using solid state detectors can reduce the incident current required by two orders of magnitude.<sup>24</sup> The advantages of using a detector whose output is weighted by the energy of the photons has been analyzed in detail by R. N. Lee.<sup>25</sup> Lee's analysis points out that a quantum detector, in which the output is proportional to the number of photons, is poorly suited to appearance potential spectroscopy. The reason is that the bremsstrahlung background, above which the signal must be detected, has a spectrum that varies as the reciprocal of the photon energy.

Using an energy detector, whose output is weighted by the energy of the photons, however, effectively discriminates against the low energy bremsstrahlung photons. Lee also points out that X-ray filtration with an energy detector does not improve its performance at any energy and degrades performance in regions of low filter transmission. Thus far, an optimized soft X-ray appearance potential



spectrometer following Lee's criteria has not been constructed.

In the soft X-ray region, excited core states are actually much more likely to decay by an Auger process than by radiative recombination. It is not surprising therefore that appearance potential spectra can also be obtained from changes in the total secondary electron yield, in which case the technique is termed Auger electron appearance potential spectroscopy (AEAPS).<sup>14</sup> In all cases examined so far, the total secondary electron yield increases at the threshold for core excitation. This is not a result that could have been predicted with certainty. It means that the number of true secondary electrons produced by the decay of the core hole exceeds the number of elastically reflected electrons lost to the excitation process.<sup>26</sup>

The apparatus required to obtain the Auger electron appearance potential spectrum is shown schematically in Fig. 3. Its simplicity makes it an attractive alternative to a synchrotron. Electrons emitted thermionically from a directly heated filament are accelerated to an anode, where some pass through a small aperture and impinge on the sample. Secondary electrons from the sample are collected on the anode, which is kept at a higher potential than the sample. The current measured in the sample circuit is therefore  $I = I_p - I_s$ , where  $I_p$  is the primary current to the sample and  $I_s$  is the secondary emission current. With the anode potential fixed,  $I_p$  is constant, and changes in  $I$  accurately reflect changes in secondary emission.

The derivative of the secondary emission is obtained by the potential modulation technique.<sup>27</sup> A sinusoidal modulation is superimposed on the emitter-to-sample potential. Lock-in detection was used to synchronously detect



variations in the sample current. The resolution requirements of extended fine structure analysis are relatively relaxed and a sizeable modulation can be employed ( $\sim 3V$  r.m.s.).

The extended fine structure is generally quite weak compared to the near-edge structure. It is therefore necessary to operate at relatively high gains, which seriously complicates the problem of background variations. To further suppress these variations, it is generally desirable to use the second derivative. This is achieved in the potential modulation technique by detecting the second harmonic of the modulation frequency.

An example of the second-derivative AEAPS spectrum is shown in Fig. 4. The near-edge L-shell spectra of Ti and Ni are clearly observed but the extended fine structure is barely detectable at this gain. The large structure at low energies is a consequence of diffraction of the incident electron beam which modulates the reflectivity.<sup>28</sup> In more crystalline samples this structure persists to many hundreds of electron volts, frequently obscuring appearance potential features. This is the most serious limitation of the AEAPS technique. Diffraction of the incident electron beam, however, has only a negligible effect on the X-ray yield. For this reason it is likely that increased attention will be given to the use of sensitive detection method in SXAPS.

### ANALYSIS

The modulation of the absorption coefficient  $N_Y(k)$  is described by

$$\chi(k) = -k^{-1} \sum_1 A_1(k) \sin [2kR_1 + \phi_1(k)] \quad (5)$$

where

$$A_1(k) = (N_1/R_1^2) |f_1(\pi, k)| \exp (-2\sigma_1^2 k^2 - 2R_1/\lambda).$$

$N_1$  is the number of atoms at a distance  $R_1$  from the absorbing atom,  $|f_1(\pi, k)|$  is the amplitude for scattering through an angle  $\pi$ , and  $\sigma_1^2$  describes the mean-square displacement of the atoms from their average positions.  $\lambda$  is the mean free path for inelastic scattering. The phase shift  $\phi(k)$  is due to the influence of the potentials of the absorbing atom and the scattering atoms on the electron wave.

The most general method of analysis is to take the Fourier transform of  $\chi(k)$  in momentum space. The transformation from energy to momentum space is given by

$$\hbar^2 k^2 / 2m = E(k) - E_0(k) \quad (6)$$

where  $E(k)$  is the energy of the photoelectron measured from the excitation threshold, and  $E_0(k)$  is the inner potential. The problem of determining  $E_0$  is the same as that faced in LEED analysis. In EXAFS, however, Stern, Sayers, and Lytle report that the result is insensitive to a reasonable choice of  $E_0$ .<sup>29</sup> Clearly, as the need for precision increases, it will become necessary to use better values of the inner potential. Values from LEED theory should be quite adequate.

The scattering phase shift  $\phi(k)$  is not generally precisely known. The transferability of phase shifts has been emphasized by Citrin, Eisenberger and Kincaid,<sup>30</sup> who point out that it should be possible to extract phase shifts from known structures. These phase shifts can then be used in the analysis of unknown structures involving the same atoms. Multiple scattering has a relatively small effect on extended fine structure analysis when viewed from the perspective of LEED analysis.<sup>31</sup>

Since the Fourier transform method seeks only the period of modulation, it can be applied directly to extended appearance potential fine structure. Moreover, the result should be unaffected by analyzing higher derivatives of the data. Initial attempts at Fourier inversion of extended fine structure above vanadium appearance potential edges, however, met with little success.<sup>31</sup> The principal difficulty proved to be background variations,<sup>18</sup> presumably resulting from diffraction of the incident electron beam. The poorly behaved background is evident in the vanadium 2p extended appearance potential fine structure shown in Fig. 5. This spectrum is taken from the work of Elam, Cohen, Roelofs and Park. At least two methods have been used to reduce these variations. One is to do a least squares fit of the data to a third order polynomial. The values of the polynomial are then subtracted point by point from the data. A second approach is to use a simple digital filtering method. The two methods work about equally well.

The Fourier transform of the spectrum in Fig. 5, after reduction of the background, is shown in Fig. 6. The transform has been shifted  $0.3 \text{ \AA}$  to correct for the backscattering phase shift. The strongest peak agrees well with the



2.69 Å nearest-neighbor spacing of vanadium. A smaller peak at a shorter distance, is evidence that the background subtraction was incomplete. The structure at larger distances than 2.69 Å probably represents more distant neighbors, but the structure is too broad for interpretation.

Several factors may contribute to the width of the features in the Fourier transform. The limited range of the data certainly contributes some broadening. Another troublesome factor is that each of the various partial waves contributing to the scattering may have different phase shifts.

As Elam et. al.<sup>18</sup> have pointed out, there is the additional problem that the range of the data includes structure from all three L-edges. The analysis assumes that the structure is associated only with the  $L_3(2p_{3/2})$  edge. This is certainly the most intense structure, but fine structure of just half the intensity must result from the  $L_2(2p_{1/2})$  edge. This structure will be displaced by the 7.4 eV spin orbit splitting. Still weaker structure due to the  $L_1(2s)$  edge, displaced by 113.2 eV, must also be present. In principal it should be possible to take advantage of these multiple edges by a proper correlation transform.

Similar analyses have been carried out for the surfaces of polycrystalline titanium and iron.<sup>19</sup>



## CONCLUSIONS

Every new spectroscopy represents an attempt to isolate a particular physical interaction from a background of other interactions. The isolation is, of course, never perfect. Whatever side effects mask the physical phenomenon under study must, however, present information of another sort. An attempt to understand one spectroscopy thus frequently succeeds in spawning another.

Appearance potential spectroscopy was developed initially as a means of determining the elemental composition of the surface from the positions of the edges. For this purpose it has some interesting limitations, but it became clear almost at once that the shapes of the edges reveal a great deal of information about the chemical state of the atoms. It is now clear that structure far above the edges can provide information on interatomic separations.

The most important application of this latest aspect of appearance potential spectroscopy is likely to be in the study of adsorbed layers. Experience with this technique, however, is extremely limited, and it is not clear what problems will be encountered. The extreme experimental simplicity, however, provides ample motivation for dealing with the complexities that may arise.

#### ACKNOWLEDGEMENT

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#### FIGURE CAPTIONS

1. Extended fine structure above the  $L_3$  and the  $L_2$  soft X-ray appearance potential thresholds of clean and oxidized chromium surfaces. The figure is taken from a 1971 paper by Houston and Park (ref. 11) and is reproduced with permission.
2. Energy level diagram contrasting X-ray absorption spectroscopy and appearance potential spectroscopy. The threshold occurs when the incident photon energy,  $E_0$ , is equal to the core electron binding energy  $E_B$ . For greater photon energies, the core electron is excited to a state  $\epsilon = h\nu - E_B$  above the Fermi energy. In appearance potential spectroscopy the excess energy is divided between two electrons, such that  $\epsilon_1 + \epsilon_2 = E_0 - E_B$ .
3. Schematic of the apparatus used for Auger electron appearance potential spectroscopy. Electrons emitted from a hot filament, are accelerated past an anode, and impinge on the sample. With constant anode voltage  $V_0$ , the current to the sample is constant. Since  $V_0$  is kept larger than the accelerating potential  $V$ , secondary electrons are collected by the anode, and the sample current is the constant primary current minus the secondary yield. A small modulation on the filament potential is used in differentiation of the sample current.

4. Second derivative Auger electron appearance potential spectrum of the clean surface of  $TiN_1$ . The large peaks at the  $2p_{3/2}$ ,  $2p_{1/2}$ , and  $2s$  thresholds correspond to excitations to the unfilled  $3d$  states. The large structure at low energies is a consequence of diffraction of the incident electron beam. In more crystalline materials the diffraction structure is even more pronounced.

5. Extended fine structure in the range 130eV to 570 eV above the  $2p_{3/2}$  appearance potential edge of clean vanadium ( the edge is at 508 volts). The spectrum represents the second derivative of the sample current at a function of the incident electron accelerating potential. (Reprinted from reference 18, with permission.)

6. Magnitude of the Fourier transform of the vanadium extended fine structure after background suppression. The arrows are the expected peak positions corresponding to atomic separations in bulk vanadium assuming a  $0.3\text{\AA}$  backscattering phase shift. The nearest neighbor peak is in good agreement. The unphysical peak at about  $1.2\text{\AA}$  is evidence that the background is not entirely removed. (Reprinted with permission from reference 18.)

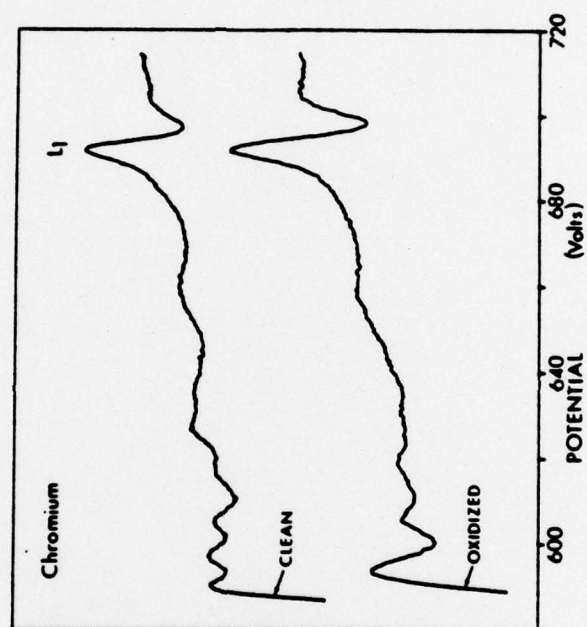


FIGURE 1



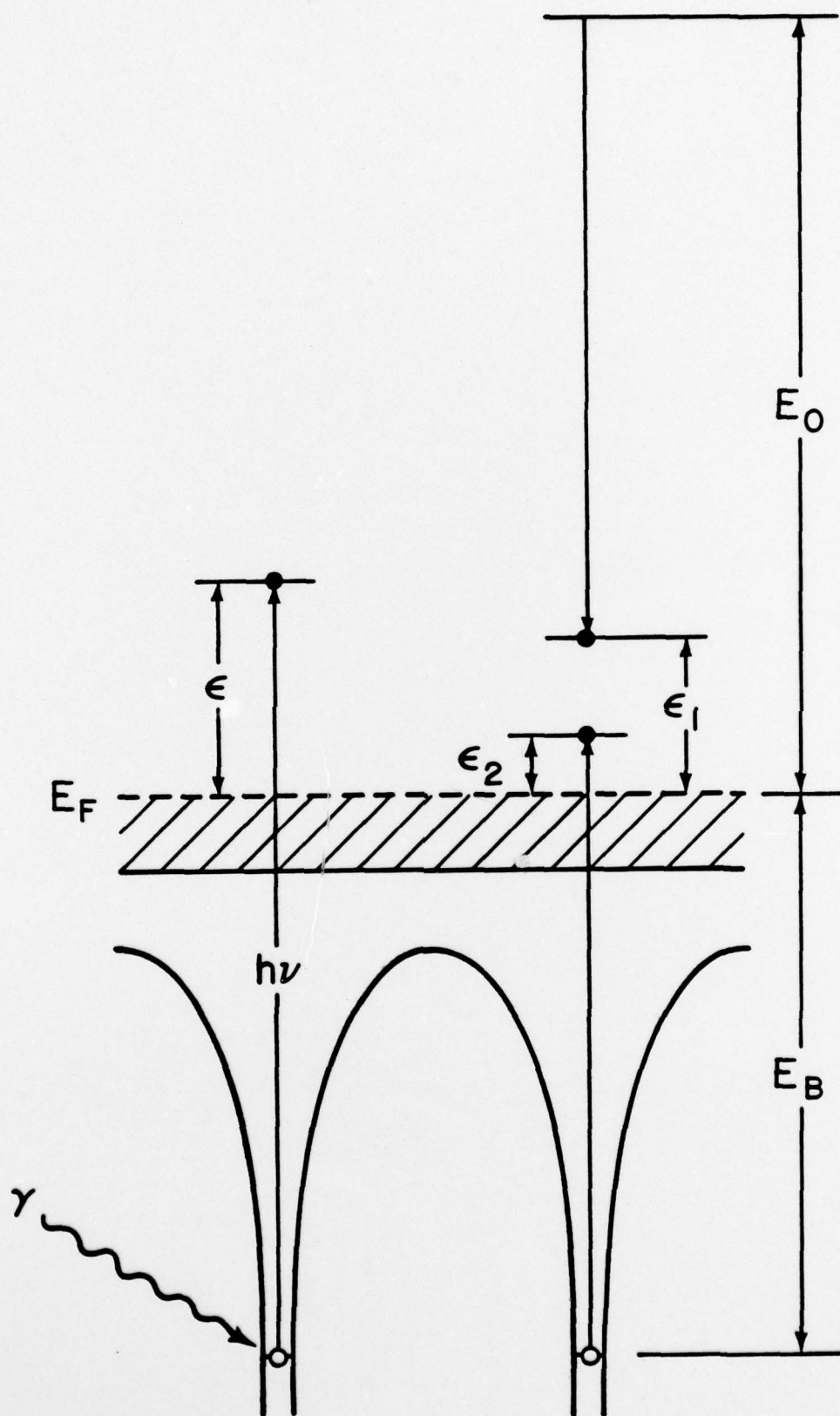


FIGURE 2

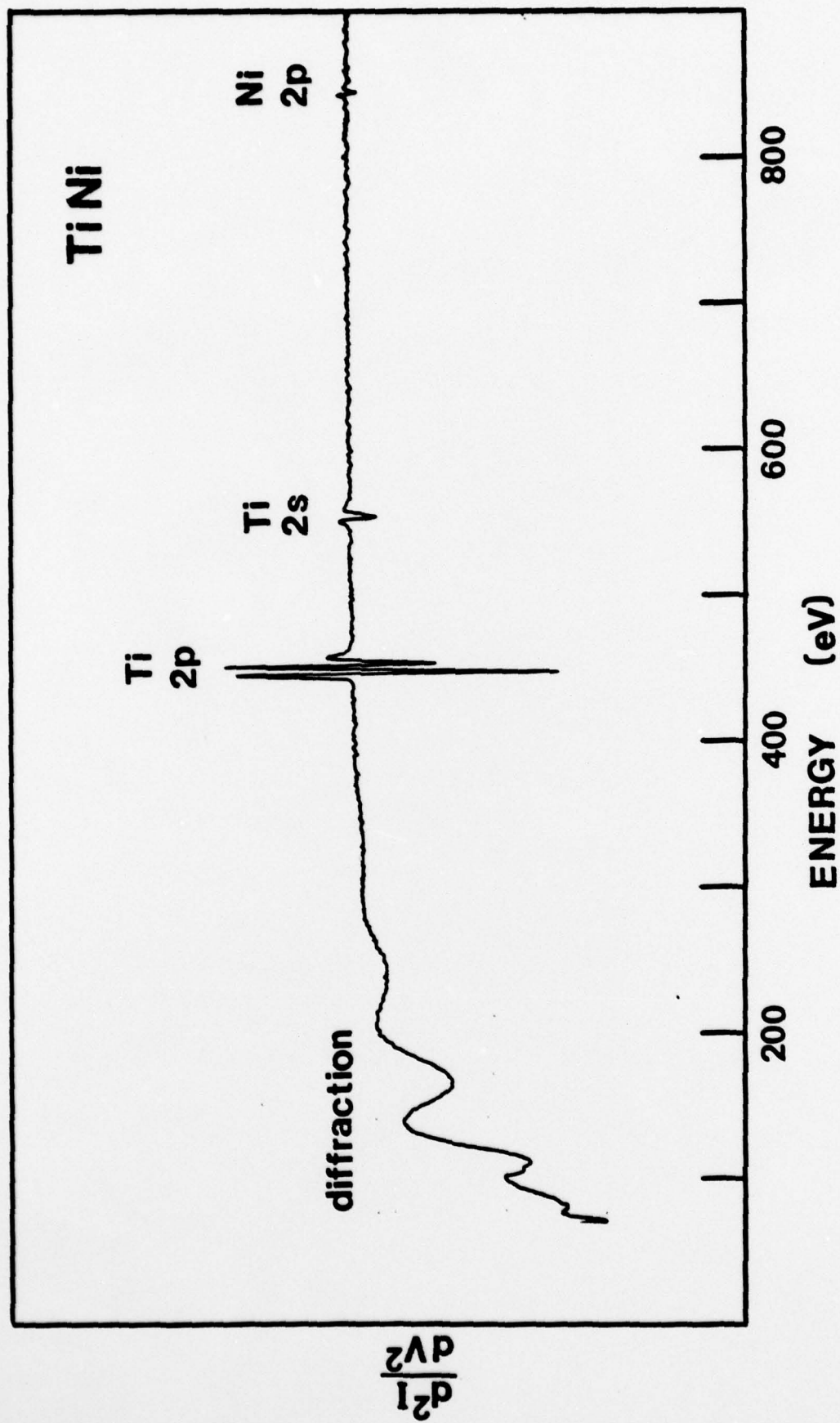


FIGURE 4

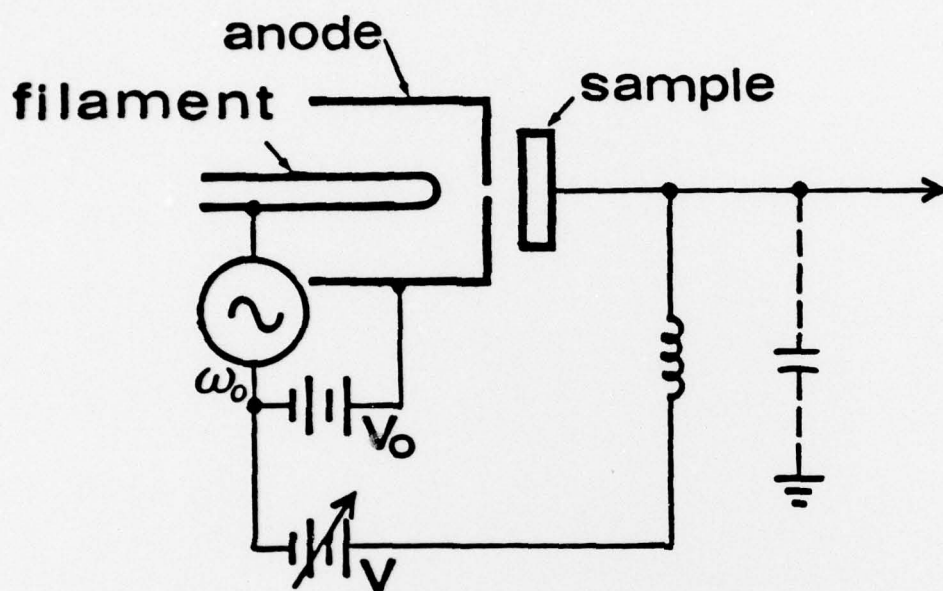
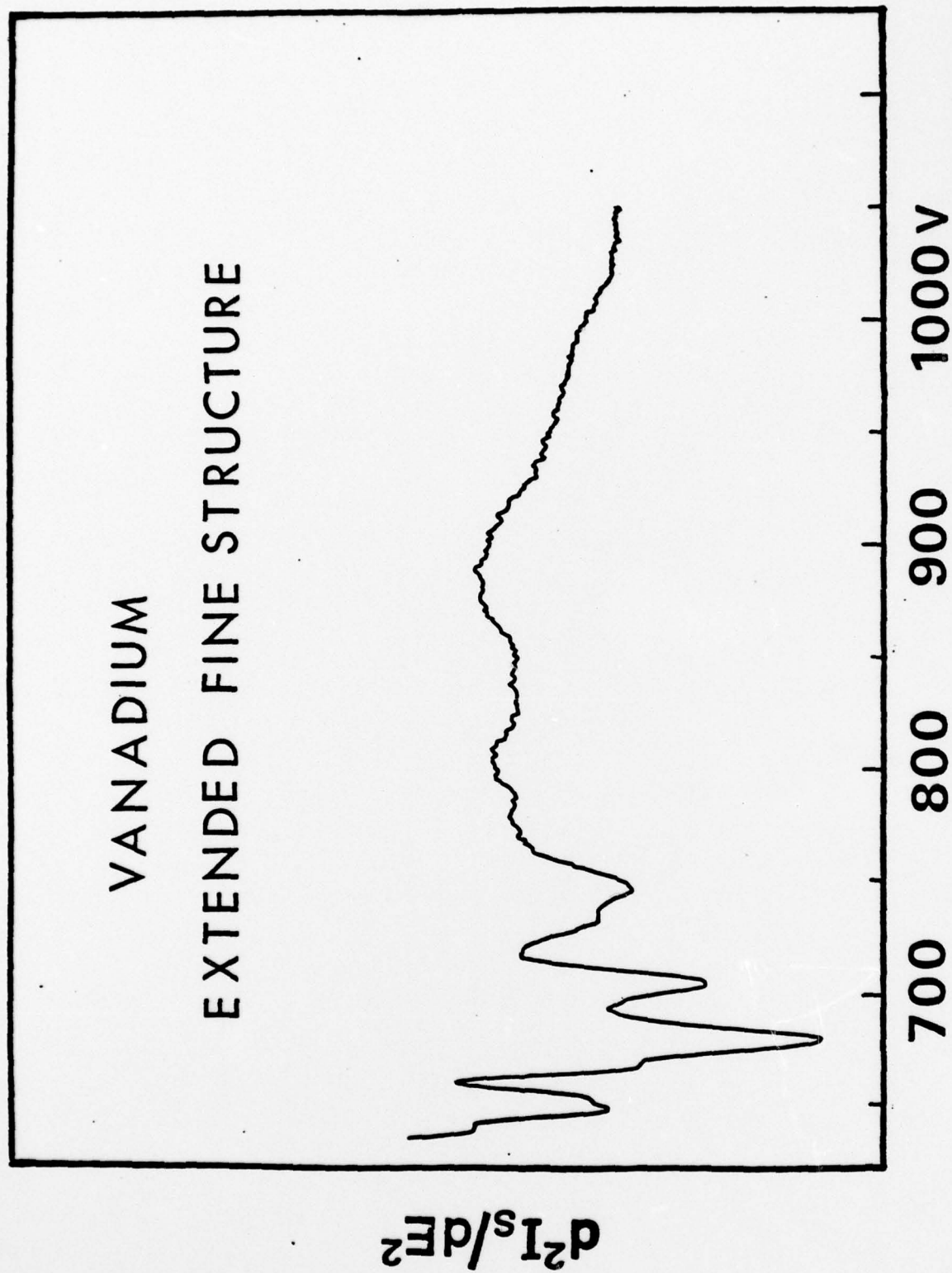


FIGURE 3





ACCELERATING POTENTIAL

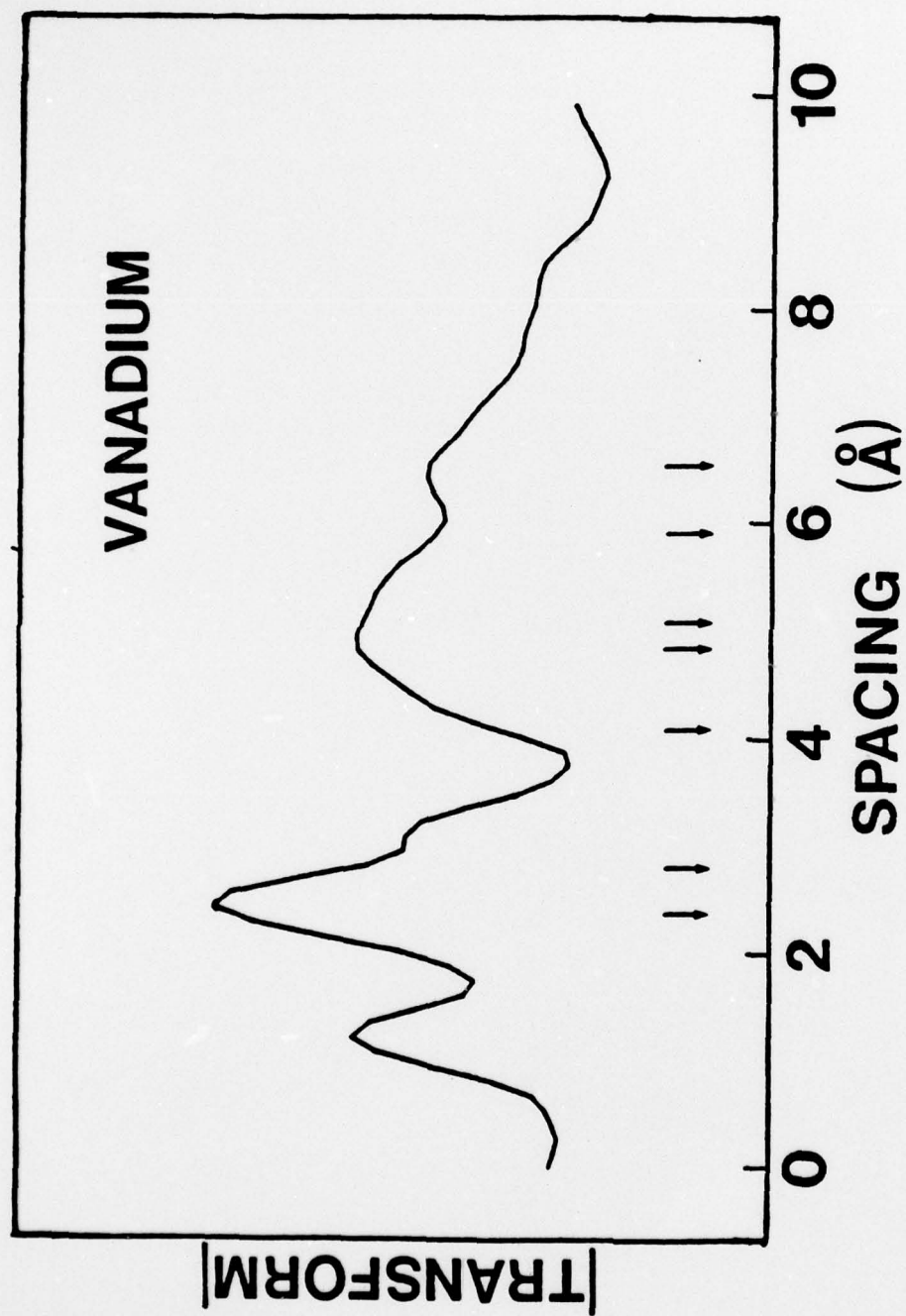


FIGURE 6